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Process for producing new polymers based on oil of cashew-nutshells, and products obtained therefrom

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(71) Applicant(s)
Martin Ernst Stielau

(72) Inventor(s)
Martin Ernst Stielau

(74) Agent/Attorney
SPRUSON and FERGUSON,GPO Box 3898,SYDNEY NSW 2001

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(71)(72) Déposant et inventeur: STIELAU, Martin, Ernst [DE/PT];
Melides, Caveira, P-7570 Grândola (PT).

(74) Mandataire: CRUZ, Jorge, Afonso; Rua Vitor Cordon, 14-3º,
P-1200 Lisbonne (PT).

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(54) Title: PROCESS FOR PRODUCING NEW POLYMERS BASED ON OIL OF CASHEW-NUT SHELLS, AND PRODUCTS OBTAINED THEREFROM

(54) Titre: PROCEDE DE FABRICATION DE NOUVEAUX POLYMERES A BASE D'HUILE DE COQUILLE DE NOIX DE CAJOU ET LES PRODUITS QUI EN RESULTENT

(57) Abstract

The present invention relates to processes and products which have been obtained with, on the one hand, a natural component which is oil of cashew-nut shell and, on the other hand, di- and/or polyisocyanates. Since the oil is comprised of a mixture of a biphenol and a fatty acid, both having a benzene ring with phenol group and side chains with one to three double bonds, the isocyanates may react three different levels: a) the COOH of the acid; b) the phenolic OH; c) the double bond of the chains.

(57) Abrégé

La présente invention traite des procédés et des produits qui ont été réalisés avec d'une part un composant naturel qui est l'huile de coquille de noix de cajou et d'autre part des di- et/ou polyisocyanates. Vu que l'huile est composée d'un mélange entre un biphenol et un acide gras, les deux ayant un anneau benzénique avec groupement phénolique et des chaînes latérales avec une à trois doubles liaisons, les isocyanates peuvent réagir sur trois niveaux différents: a) celui des COOH de l'acide, b) celui des OH phénoliques et finalement, c) celui des doubles liaisons des chaînes.

SPECIFICATION

"PROCESS FOR MANUFACTURING NEW POLYMERS MADE FROM CASHEW NUT SHELL OIL AND THE PRODUCTS OBTAINED THEREFROM"

Application fields

The present invention concerns polymers made of cashew nut shell oil (hereinafter referred to as CNSO), which together with di- and/or polyisocyanates can constitute many different molecular structures.

Prior art

CNSO is a by-product of the cashew nut preparation food industry.

This liquid, which is found in the shell of the nut and is released when the shell is opened, is a 9:1 mixture of a fatty acid (anacardic acid, which has one phenyl radical at the benzenoid ring) and a diphenol (Cardol); both with side chains with 15 carbon and 27 hydrogen atoms and one with three double bonds.

The current uses of this product are mainly in the field of phenoplastics, where, by neglecting the double bonds of the chains:

- the fatty acid is decarboxylated with a small quantity of sulphuric acid;

- the phenyl radicals are then reacted with aldehydes. The results are products characterised by their great resistance to heat and abrasion.

Showa's Japanese patent n° 33-27 905 of 1st October 1958 contains a new application for this product by reacting it with di- and/or polyisocyanates. This method of manufacturing polyurethane, owing to a reaction between the CNSO and a polyisocyanate, demonstrates the possibility of dimerising the CNSO in the presence of a polymerisation catalyst at temperatures of up to 140°C. The result of this method is a product with high viscosity, which has to be washed and dried before it is used practically with isocyanates.

German patent n° 2152 606 of 22nd October 1971, belonging to Bayer AG, shows in the context of a process for the internal plastification of an epoxy resin, that phenyl radicals can be used to temporarily block the NCO radicals from the excess polyisocyanates of the prepolymers. After a subsequent reaction, when tertiary amines take the place of the phenyls, these remain free in the final product.

Contents of the invention

The present invention demonstrates a simpler way of manufacturing polymers made of CNSO and a cleaner way of manufacturing products with blocked NCO radicals, by linking up the free phenyl radicals to an available aldehyde. Thanks to the processes invented, it is possible to manufacture products as varied as rigid foam, elastomers, thermoplastic rubber or single-component resins without solvents.

According to a first embodiment of this invention, there is provided a process for manufacturing a component of a plastic material made of CNSO, the phenyl radicals of which are temporarily blocked by NCO radicals of a di- and/or polyisocyanate, characterised by:

- 5 a) the complete decarboxylation of the CNSO;
- b) the addition of an equivalent quantity of TDI before dimerisation of the CNSO by heating; and
- c) renewed heating until the isocyanate is entirely blocked.

According to a second embodiment of this invention, there is provided a process for
10 manufacturing a component of a plastic material made of CNSO which precondenses with an aldehyde, and characterised by:

- a) the heating of the CNSO with a small quantity of triethylamine up to approximately 170°C;
- b) the addition of an equivalent quantity of an aldehyde; and
- 15 c) renewed heating until condensation begins.

According to a third embodiment of this invention, there is provided a process for manufacturing a polymer, characterised by the fact that a di- and/or polyisocyanate reacts with CNSO which has been previously decarboxylated before heating at a temperature higher than 140°C.

- 20 According to a fourth embodiment of this invention, there is provided a process for manufacturing rigid foam, characterised by the fact that a di- and/or polyisocyanate reacts with CNSO, the chemical structure of which has not been essentially modified.



Description of the invention

CNSO can, together with the polyisocyanates, react on three different levels:

1. The COOH of the fatty acid, following the Würtz reaction:



2. The double bonds of the side chains, and
3. The phenyl radicals of the rings.

The first level is always interesting when a product is intended to be expanded. Thus, with the simultaneous attack of a polyisocyanate on the three levels, a rigid foam of excellent quality can be obtained. Different components which can be polymerised can be obtained either by simply heating the CNSO or by the following method: add a small quantity of diluted sulphuric acid to the CNSO and heat. At around 130°C, the CO₂ of the carboxyl is released. By heating further, concentration and dimerisation increase. By adding a polyisocyanate, more or less reticulated products are obtained.

In relation to the above-mentioned Bayer patent and the possibility of temporarily blocking the NCO radicals of an isocyanate, the following method is used: CNSO is heated up to 180°C with a small quantity of diluted sulphuric acid, it is left to cool down to 120°C and then an equivalent quantity of TDI is added. This mixture is kept at 80°C until there is no more free isocyanate.

Starting with such a product and adding a second one, it is easy to manufacture a single-component glue.

This second component would be, for example, a mixture of CNSO and Furfural, which had been heated beforehand with a small quantity of triethylamine and then cooled down to room temperature. (It has been discovered that such a mixture remains stable at this temperature.)

If the quantity of Furfural in the second mixture corresponds to the total quantity of decarboxylated CNSO and the mixture of the first preparation is heated up with the mixture of the second preparation to a temperature higher than 150°C, then the initially blocked NCO radicals will be released and react with the COOH of the second preparation. The phenyl radicals react with the Furfural and give a very brilliant, hard but nevertheless flexible product.

As in the Bayer patent, the preparation with the blocked isocyanate can be used to flexibilize epoxy resins or, by heating it up, to make elastic products.

As explained in the example below, an equivalent mixture of CNSO and Furfural can be used as a component for the manufacture of a rigid foam, provided that a polyisocyanate can react beforehand with the OH of the CNSO carboxyls.

Example 1

A mixture of 100g of CNSO and 28g of Furfural is heated up to 150°C. This is quickly mixed with either 32g of TDI or 49g of MDI, resulting in expansion, reticulation and hardening. The resulting rigid foam acquires its final characteristics after a few days.

Example 2

Here follows the quantification of the manufacture of the above-mentioned single-component glue.

A first mixture of 34g of CNSO and 19g of Furfural is heated up to 150°C, while stirring.

A second mixture containing 34g of CNSO and 0.68g of sulphuric acid (50%) is heated up to 170°C, cooled down to 110°C and completed with 7g of TDI. It is stirred slowly for 4 hours under nitrogen at a temperature of 70°C and then cooled down.

By mixing the first preparation with the second one, a stable liquid is obtained, which has a temperature higher than 140°C, when the NCO radicals are released from the phenyl radicals and can react with the COOH of the CNSO from the first mixture. The free phenyl radicals react with the rest of the Furfural from the first mixture.

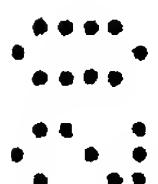
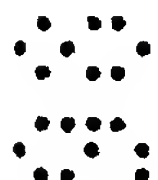
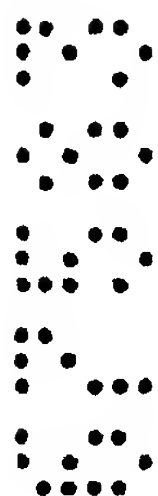
Example 3

In order to produce rigid foam, 100g of CNSO are mixed with 90g of MDI. The exothermic reaction and expansion are almost immediate. Hardening occurs about an hour later, depending on the temperature.

Example 4

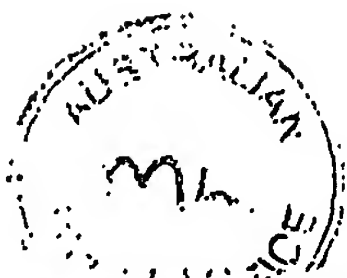
100g of CNSO are heated up to 300°C then

cooled down to room temperature 40g of MDI are added and the preparation is mixed well. After the exothermic reaction, a duromer of good mechanical and chemical resistance is obtained.



The claims defining the invention are as follows:

1. Process for manufacturing a component of a plastic material made of CNSO, the phenyl radicals of which are temporarily blocked by NCO radicals of a di- and/or polyisocyanate, characterised by:
 - 5 a) the complete decarboxylation of the CNSO;
 - b) the addition of an equivalent quantity of TDI before dimerisation of the CNSO by heating; and
 - c) renewed heating until the isocyanate is entirely blocked.
2. A process according to claim 1 characterised in that the CNSO is
 10 decarboxylated by the addition of a small quantity of diluted sulphuric acid.
3. Process for manufacturing a component of a plastic material made of CNSO which precondenses with an aldehyde, and characterised by:
 - a) the heating of the CNSO with a small quantity of triethylamine up to approximately 170°C;
 - 15 b) the addition of an equivalent quantity of an aldehyde; and
 - c) renewed heating until condensation begins.
4. A process according to claim 3 characterised in that the aldehyde is furfural.
5. Process according to any one of claims 1 to 4 which consists in mixing equivalent quantities of the component according to claim 1 or claim 2. with the
 20 component according to claim 3 or claim 4.
6. Process for manufacturing a component of a plastic material made of CNSO, substantially as hereinbefore described with reference to any one of the Examples.
7. A component of a plastic material manufactured by the process of any one of claims 1 to 6.
- 25 8. Components that can be hardened made in accordance with the process according to any one of claims 1 to 6.
9. Process for manufacturing a polymer, characterised by the fact that a di- and/or polyisocyanate reacts with CNSO which has been previously decarboxylated before heating at a temperature higher than 140°C.
- 30 10. A process according to claim 9 characterised in that the CNSO is decarboxylated by adding a small quantity of sulfuric acid.
11. Process for manufacturing a polymer, characterised by the fact that a di- and/or polyisocyanate reacts with CNSO after this CNSO has been treated mainly by heating.
- 35 12. Process for manufacturing a polymer, substantially as hereinbefore described with reference to any one of the Examples.
13. A polymer manufactured by the process according to any one of claims 9 to 12.



14. Process for manufacturing rigid foam, characterised by the fact that a di- and/or polyisocyanate reacts with CNSO, the chemical structure of which has not been essentially modified.

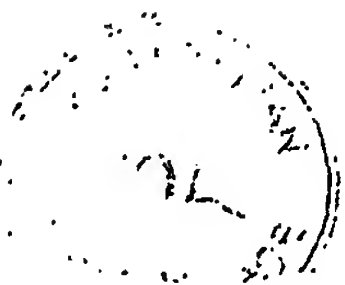
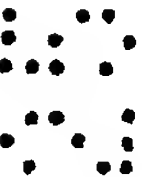
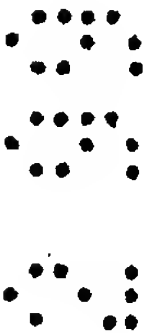
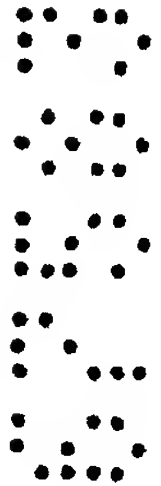
15. A process according to claim 14 characterised in that both the phenolic OH groups and the carboxylic OH groups are available to react with the NCO groups of the polyisocyanate.

16. Process for manufacturing rigid foam, substantially as hereinbefore described with reference to any one of the Examples.

17. Rigid foam manufactured by the process according to any one of claims 14 to 16.

Dated 25 February, 1999
Martin Ernst Stielau

Patent Attorneys for the Applicant/Nominated Person
SPRUSON & FERGUSON



ABSTRACT

The present invention relates to processes and products made of a natural component being cashew nut shell oil (CNSO) and another component being di- and/or polyisocyanates. Since the CNSO is a mixture of a biphenol and a fatty acid, both of which have a benzenoid ring with phenyl radicals and side chains, one of which has three double bonds, the isocyanates can react on three different levels:

- I. The COOH of the fatty acid
- II. The OH of the phenyl radicals
- III. The double bonds of the chains.

